# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-151046
(43)Date of publication of application : 30.05.2000

(51)Int.Cl. H05K 1/03
B32B 15/08
B32B 27/34
C08G 73/10
C08J 7/04
// C08L 79:08

(21)Application number : 10-314186
(22)Date of filing : 05.11.1998

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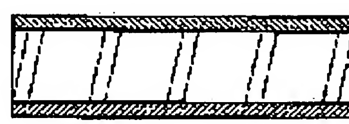
## (54) POLYIMIDE FILM AND FLEXIBLE BOAR

(57)Abstract:
PROBLEM TO BE SOLVED: To improve adhesion between a polyimide film suited to flexible boards and a metal thin film formed thereon by a dry process and suppress curling, irrespective of the heat history.
SOLUTION: A polyimide film for constituting an insulation layer of a flexible board composed of this insulation layer laid on a conductor layer has a three- layer structure composed of a first, second and third polyimide layers 1, 2, 3, the second layer 2 uses one having approximately the same thermal linear expansion coefficient as the conductor, and the first polyimide layer 1 adjacent the conductor layer is made of sulfo group-contg. polyimide.




LEGAL STATUS

| | |
|---|---|
| [Date of request for examination] | 13.06.2000 |
| [Date of sending the examiner's decision of rejection] | |
| [Kind of final disposal of application other than the examiner's decision of rejection or application converted registration] | |
| [Date of final disposal for application] | |
| [Patent number] | 3641952 |
| [Date of registration] | 04.02.2005 |
| [Number of appeal against examiner's decision of rejection] | |
| [Date of requesting appeal against examiner's | |

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CLAIMS

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[Claim(s)]
[Claim 1] The 2nd polyimide layer which is a polyimide film for constituting the insulating layer concerned of the flexible substrate with which it comes to arrange an insulating layer on a conductor layer, has the three-tiered structure of the 1st polyimide layer, the 2nd polyimide layer, and the 3rd polyimide layer, and is located in those centers is a polyimide film with which the 1st polyimide layer arranged in the side which has the heat ray expansion coefficient of a conductor layer and abbreviation identitas, and touches a conductor layer consists of sulfone radical content polyimide.
[Claim 2] The polyimide film according to claim 1 with which the 3rd polyimide layer consists of sulfone radical content polyimide.
[Claim 3] The polyimide film according to claim 1 or 2 whose heat ray expansion coefficients of the 2nd polyimide layer are 10x10-6/K - 25x10-6/K.
[Claim 4] The polyimide film according to claim 1 or 2 whose absolute values of the difference of the heat ray expansion coefficient of the 1st polyimide layer and the 3rd polyimide layer are less than 3x10-6/K.
[Claim 5] Sulfone radical content polyimide is guided from acid 2 anhydride and diamine, and they are acid 2 anhydride and the polyimide film of diamine according to claim 1 or 2 with which a sulfone radical exists in either at least.
[Claim 6] The polyimide film according to claim 5 with which a sulfone radical exists in acid 2 anhydride and the both sides of diamine.
[Claim 7] The flexible substrate characterized by preparing the conductor layer which consists of a metal thin film formed in the 1st polyimide layer side front face of a polyimide film according to claim 1 to 6 of the dry process, and an electrolysis plated-metal layer formed on the metal thin film.
[Claim 8] The flexible substrate with which the conductive layer is prepared in the 1st polyimide layer side front face of a polyimide film according to claim 2 to 6, and the 3rd polyimide layer side front face.
[Claim 9] The flexible substrate according to claim 7 or 8 which has the two-layer structure of a nickel-Cu thin film / copper thin film where the metal thin film was formed of the spatter process.
[Claim 10] The flexible substrate according to claim 9 whose electrolysis plated-metal layer is an electrolytic copper deposit.

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[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the flexible substrate using a polyimide film and it useful as the insulating base of a flexible substrate.
[0002]
[Description of the Prior Art] The approach of forming a metal deposit as a conductor layer according to wet process as the general production approach of a flexible substrate on the polyimide film which is an insulating layer is mentioned. Here, the commercial item of the monolayer structure where the polyimide film was guided from acid 2 anhydride and diamines (pyromellitic acid 2 anhydride / diamino diphenyl ether, diphenyl tetracarboxylic dianhydride / p phenylenediamine, etc.) is used widely.
[0003] By the way, since its adhesion with a metal deposit is not enough if the polyimide film of marketing of monolayer structure remains as it is, in advance of formation of a metal deposit, surface treatment is performed in strong-base nature water solutions, such as a potassium-hydroxide water solution and a hydrazine water solution. however, the thing for which surface treatment is controlled to be in a fixed surface state -- very much -- difficult -- moreover -- generating and a lot of wastewater of harmful gas -- it is necessary to process -- a high -- the cost antipollution measure is needed.
[0004] Then, for dry processes with comparatively easy control (for example, glow discharge processing, plasma electrodischarge treatment, ion beam exposure processing, plasma excitation reactivity ion irradiation, etc.) to perform surface treatment of the polyimide film of marketing of monolayer structure, to form a metal thin film on a polyimide film according to dry processes, such as a spatter, succeedingly, and to form an electrolysis plated-metal layer according to wet process (electrolysis plating) on it further is tried.

[0005]
[Problem(s) to be Solved by the Invention] However, when a dry process performed surface treatment of a polyimide film, there was a problem that the adhesion of the dry process processing front face of the polyimide film of marketing of monolayer structure and a metal thin film was not enough.
[0006] Moreover, the produced flexible substrate curled and there was a case where trouble was caused to component mounting.
[0007] This invention aims at solving the trouble of the above Prior art, and raising the adhesion between the polyimide film suitable for a flexible substrate, and the metal thin film formed of a dry process on it, and controlling generating of curl.
[0008]
[Means for Solving the Problem] By this invention person's making a polyimide film a three-tiered structure, and using what has a heat ray expansion coefficient almost equivalent to the heat ray expansion coefficient of the conductor layer formed on a polyimide film as a polyimide layer of those centers By not being based on the contents of the heat history in the usual flexible substrate production process, but being able to control curl generating of a flexible substrate, and constituting the polyimide layer of the side which moreover touches a metal thin film from sulfone radical content polyimide It came to complete a header and this invention for the ability of the adhesion between a polyimide film and a metal thin film to be raised.
[0009] That is, this invention is a polyimide film for constituting the insulating layer concerned of the flexible substrate with which it comes to arrange an insulating layer on a conductor layer, and it has the three-tiered structure of the 1st polyimide layer, the 2nd polyimide layer, and the 3rd polyimide layer, and the 2nd polyimide layer located in those centers has the heat ray expansion coefficient of a conductor layer and abbreviation identitas, and offers the polyimide film with which the 1st polyimide layer arranged in the

side which touches a conductor layer consists of sulfone radical content polyimide.
[0010]
[Embodiment of the Invention] Hereafter, this invention is explained to a detail.
[0011] The polyimide film of this invention is a polyimide film for constituting the insulating layer concerned of the flexible substrate with which it comes to arrange an insulating layer on a conductor layer, and as shown in drawing 1 , it has the three-tiered structure of the 1st polyimide layer 1, the 2nd polyimide layer 2, and the 3rd polyimide layer 3.
[0012] In this invention, what has the heat ray expansion coefficient of a conductor layer and abbreviation identitas is used as the 2nd polyimide layer 2 of the center currently pinched by the 1st polyimide layer 1 and the 3rd polyimide layer 3. Thereby, it cannot be based on the contents of the usual heat histories (ordinary temperature preservation, solder DIP processing, etc.), but curl generating of a flexible substrate can be controlled.
[0013] It is preferably desirable x(10-25) 10-6/K, and to adjust more preferably the heat ray expansion coefficient of the 2nd polyimide layer 2 to x(18-23) 10-6/K in view of the point which is the numeric value the heat ray expansion coefficient of the conductor generally used to a flexible substrate is indicated to be to Table 1.
[0014] Moreover, as for the heat ray expansion coefficient of the 1st polyimide layer 1 and the 3rd polyimide layer 3, it is desirable that the absolute values of the point the effectiveness's [ which controls curl ] to both difference are less than 3x10-6/K. Even if it may be the same, of course and is almost the same as that of the 2nd polyimide layer 2, it does not interfere at all.
[0015]
[Table 1]

| | 熱線膨張係数（×１０$^{-6}$／K） | |
|---|---|---|
| 材質 | 文献値 | 実測値 |
| 銅箔 | １６～２０ | １８～１９ |
| ＳＵＳ３０４箔 | １６～１７ | １７～１８ |
| ＳＵＳ４３０箔 | １０～１１ | − |
| アルミニウム箔 | ２２～２５ | ２２～２３ |
| ベリリウム銅箔 | １７～１８ | − |
| リン青銅箔 | １７～１８ | − |

[0016] Moreover, in the polyimide film of this invention, the 1st polyimide layer 1 of the side which touches a conductor layer consists of sulfone radical content polyimide. By existence of a sulfone radical, the adhesion force between it and a metal thin film can be raised. And the adhesion stabilized also by the usual heat history is securable.
[0017] In addition, since the heat ray expansion coefficient can be easily made into the heat ray expansion coefficient of the 1st polyimide layer 1 at abbreviation identitas and a metal thin film can moreover be formed by good adhesion also on the 3rd polyimide layer 3 when the 3rd polyimide layer 3 is also constituted from sulfone radical content polyimide, it is desirable when manufacturing a double-sided flexible substrate.
[0018] Here, as sulfone radical content polyimide, what was guided from acid 2 anhydride and diamine can be used preferably, and the sulfone radical originates in acid 2 anhydride and the sulfone radical of diamine which exists in either beforehand at least. The sulfone radical content polyimide obtained when a sulfone radical exists in acid 2 anhydride and the both sides of diamine especially can be used preferably.
[0019] As an example of acid 2 anhydride, pyromellitic acid 2 anhydride (PMDA), 3 and 4, 3', and 4'-biphenyl tetracarboxylic dianhydride (BPDA), 3 and 4, 3', and 4'-benzophenone tetracarboxylic dianhydride (BTDA), 3, 3', 4, and 4'-diphenylsulfone tetracarboxylic dianhydride (DSDA) is mentioned preferably.
[0020] As an example of diamine, 4 and 4'-diamino diphenyl ether (DPE), p phenylenediamine (PDA), 4, and 4'-diamino benzanilide (DABA), 4, and 4'-bis(p-amino phenoxy) diphenylsulfone (BAPS) is mentioned preferably.
[0021] It is desirable that the thickness of the 2nd polyimide layer 2 is thicker than the 1st polyimide layer 1 and the 3rd polyimide layer 3 about the thickness of the 1st polyimide layer 1, the 2nd polyimide layer 2, and the 3rd polyimide layer 3. Since as for the thickness of the 2nd polyimide layer it will become difficult

to store a heat ray expansion coefficient in the range of x(10-25) 10-6/K if too thin, the polyimide film itself will become hard if too thick, and the roll volume of predetermined magnitude becomes impossible, specifically, it is preferably set to 10-200 micrometers. moreover -- if the thickness of the 1st polyimide layer 1 and the 3rd polyimide layer 3 is too thin -- forming membranes -- being hard -- since the heat ray expansion coefficient of the whole polyimide film for which it is made to depend on the heat ray expansion coefficient of the 2nd polyimide layer 2, the heat ray expansion coefficient of a conductor, and a difference may become large if too thick, it may be 1-10 micrometers preferably.

[0022] the polyimide film of this invention as shown in drawing 1 -- the one side -- or when the 3rd polyimide layer 3 is also constituted from sulfone radical content polyimide, it becomes an one side or double-sided flexible substrate, respectively by preparing the conductor layer which consists of an electrolysis plated-metal layer formed on the metal thin film formed in the both sides of the dry process, and its metal thin film.

[0023] this flexible substrate -- a sulfone radical content polyimide layer (only the 1st polyimide layers are both layers of the 1st polyimide layer and the 3rd polyimide layer) -- a front face -- existing -- the interior -- a conductor layer and abbreviation -- since the polyimide film of this invention which has the polyimide layer (the 2nd polyimide layer) of the same heat ray expansion coefficient is used, the adhesion of the metal thin film formed of a dry process will become good also to the usual heat history. And since the heat ray expansion coefficient of the 2nd polyimide layer which specifies substantially the heat ray expansion coefficient of the whole polyimide film is almost the same as that of it of a conductor layer, generating of the curl in ordinary temperature and component-mounting temperature can be controlled greatly.

[0024] Although a metal thin film is formed of a dry process, the general physical vapor deposition (for example, a vacuum deposition process, an ion plating process, a spatter process, etc.) as a dry process can be used.

[0025] As a metal thin film, the thin film of nickel, Co, Cr, Zr, Pd, Cu(s), or these alloys is desirable. When gold plate-proof nature, tinning-proof nature, etc. are especially taken into consideration, the two-layer structure thin film of the nickel-Cu thin film (50-500A thickness) / copper thin film (100-2000A thickness) formed of a spatter process is desirable.

[0026] As an electrolysis plated-metal layer, the electrolytic copper deposit of 5-50-micrometer thickness is desirable. Formation of an electrolytic copper deposit can be chosen suitably, for example, can be formed by copper sulfate bath plating of current density 0.2 - 10 A/dm2.

[0027] In addition, it is desirable to perform surface treatment processing of glow discharge processing, plasma electrodischarge treatment (gas or mixed-gas ambient atmospheres, such as nitrogen oxide gas, oxygen, and an argon), UV irradiation processing, etc., etc. to the front face of a polyimide film in advance of formation of a metal thin film from the point which raises adhesion.

[0028] Below, the example of manufacture of the polyimide film of this invention is explained.

[0029] First, coating of the polyamic acid varnish for the 1st polyimide stratification is carried out by a T die etc. on the exfoliation bases (for example, a stainless steel steel drum or a belt, a heat-resistant-resin exfoliation sheet, a metallic foil, etc.), it is dried at about 80-140 degrees C so that it may fall within the range whose volatile-matter contents (water produced by the solvent or condensation) are 7 - 50 % of the weight, and the polyamic acid film for the 1st polyimide stratification is produced.

[0030] When it means that imide-ization is advancing too much that a volatile matter content is less than 7 % of the weight here, there is a possibility that adhesion with the 2nd polyimide layer may become inadequate and it exceeds 50 % of the weight, it foams at the time of final imide-izing, and there is a possibility that the polyimide film of the desired engine performance may not be obtained.

[0031] Next, on the polyamic acid film for the 1st polyimide stratification, coating of the polyamic acid varnish for the 2nd polyimide stratification is carried out similarly, it dries at about 80-140 degrees C so that it may be settled at within the limits whose volatile matter content is 7 - 50 % of the weight, and the polyamic acid film for the 2nd polyimide stratification is produced.

[0032] Next, on the polyamic acid film for the 2nd polyimide stratification, coating of the polyamic acid varnish for the 3rd polyimide stratification is carried out similarly, it dries at about 80-140 degrees C so that it may be settled at within the limits whose volatile matter content is 7 - 50 % of the weight, and the polyamic acid film for the 3rd polyimide stratification is produced. Thereby, the polyamic acid film of a three-tiered structure is obtained.

[0033] Next, the polyimide film of this invention is obtained by exfoliating from the exfoliation base and forming the polyamic acid film of the obtained three-tiered structure into perfect imide at 230-350 degrees C under inert gas ambient atmospheres, such as nitrogen gas.

[0034] In addition, when a metallic foil is used as the exfoliation base, before exfoliating the polyamic acid film of a three-tiered structure from a metallic foil, perfect imide is formed, and a polyimide film is obtained by carrying out etching removal of the metallic foil.
[0035] The example of manufacture of an one side flexible substrate is explained below using the polyimide film of this invention.
[0036] First, a metal thin film is formed on the surface of a polyimide film according to dry processes (vacuum evaporation technique, the ion plating method, spatter, etc.).
[0037] In addition, it is desirable to perform beforehand surface treatment processings (glow discharge, plasma electrodischarge treatment, etc.) to a polyimide film front face in advance of formation of this metal thin film.
[0038] Next, an electrolysis plated-metal layer is formed on the formed metal thin film. Thereby, an one side flexible substrate is obtained. A double-sided flexible substrate is obtained by repeating the above same actuation at the polyimide film rear face.
[0039]
[Example] Hereafter, this invention is explained concretely.
[0040] P phenylenediamine (PDA, Mitsui Chemicals, Inc. make) 0.433kg (4.00 mols) and 4 and 4'-diamino diphenyl ether (made in [ Wakayama energy-ized company ] DPE) 0.801kg (4.00 mols) were dissolved in the 60l. reaction vessel with example of reference A1 (preparation of the polyamic acid varnish which used acid 2 anhydride which has a sulfone radical) jacket under nitrogen-gas-atmosphere mind at solvent N-methyl-pyrrolidone (NMP, Mitsubishi Chemical make) about 35.3kg. Then, it was made to react in 25 degrees C for 3 hours, adding gradually 2.690kg (DSDA, New Japan Chemical Co., Ltd. make) (8.08 mols) of 3, 3', 4, and 4'-diphenylsulfone tetracarboxylic dianhydride. This prepared about 10% of solid content, and the polyamic acid varnish of viscosity 20 Pa-S (25 degrees C).
[0041] After applying the obtained polyamic acid varnish on copper foil and dispersing a solvent with a 80-160-degree C continuous furnace, the temperature up of the ambient temperature was carried out to 230-350 degrees C, and at 350 degrees C, it processed for 30 minutes and imide-ized. And the monolayer polyimide film of 25-micrometer thickness was obtained by carrying out etching removal of the copper foil with a ferric chloride solution. The heat ray expansion coefficient of the obtained polyimide film (the measuring device used: thermal mechanical analyzers (TMA/SCC150CU, product made from SII (the **** method: working loads 2.5g-5g)) were 36x10-6/K.)
[0042] 4 and 4'-bis(p-amino phenoxy) diphenylsulfone (BAPS, Wakayama energy-ized company make) 3.460kg (8.00 mols) was dissolved in solvent N-methyl-pyrrolidone (NMP, Mitsubishi Chemical make) about 54.5kg under nitrogen-gas-atmosphere mind like the example A1 of example of reference A2 (preparation of polyamic acid varnish which used diamine which has sulfone radical) reference. Then, it was made to react in 25 degrees C for 3 hours, adding gradually 2.603kg (BTDA, die cel chemistry company make) (8.08 mols) of 3, 3', 4, and 4'-benzophenone tetracarboxylic dianhydride. This prepared about 10% of solid content, and the polyamic acid varnish of viscosity 15 Pa-S (25 degrees C).
[0043] The monolayer polyimide film was obtained by processing the obtained polyamic acid varnish like the example A1 of reference (heat-ray expansion coefficient: 43x10-6/K).
[0044] 4 and 4'-bis(p-amino phenoxy) diphenylsulfone (BAPS, Wakayama energy-ized company make) 3.460kg (8.00 mols) was dissolved in solvent N-methyl-pyrrolidone (NMP, Mitsubishi Chemical make) about 55.3kg under nitrogen-gas-atmosphere mind like the example A1 of the example A3 (preparation of polyamic acid varnish which used acid-anhydride [ which has a sulfone radical ], and diamine which has sulfone radical) reference of reference. Then, it was made to react in 25 degrees C for 3 hours, adding gradually 2.690kg (DSDA, New Japan Chemical Co., Ltd. make) (8.08 mols) of 3, 3'-4, and 4'-diphenylsulfone tetracarboxylic dianhydride. This prepared about 10% of solid content, and the polyamic acid varnish of viscosity 12 Pa-S (25 degrees C).
[0045] The monolayer polyimide film was obtained by processing the obtained polyamic acid varnish like the example A1 of reference (heat-ray expansion coefficient: 53x10-6/K).
[0046] A kind or two sorts of diamines (a total of 10.0 mols) shown in Table 2 were dissolved in the 60l. reaction vessel the example B1 of reference - with B6 (preparation of polyamic acid varnish for producing polyimide film with which heat ray expansion coefficients differ) jacket under nitrogen-gas-atmosphere mind at solvent N-methyl-pyrrolidone (NMP, Mitsubishi Chemical make) about 46kg. Then, it was made to react in 50 degrees C for 3 hours, adding gradually acid 2 anhydride (10.1 mols) of Table 2. This prepared the polyamic acid varnish of the viscosity of Table 2 at about 10% of solid content.
[0047] After applying the obtained polyamic acid varnish on copper foil and dispersing a solvent with a 80-

160-degree C continuous furnace, the temperature up of the ambient temperature was carried out to 230-350 degrees C, and at 350 degrees C, it processed for 30 minutes and imide-ized. And by carrying out etching removal of the copper foil with a ferric chloride solution, the monolayer polyimide film of 25-micrometer thickness in which the heat ray expansion coefficient of Table 2 is shown was obtained.
[0048] In addition, the abbreviated name of the acid 2 anhydride and diamine which were used all over Table 2 is as follows.
[0049] an acid 2 -- anhydride PMDA 4, 4'-diamino diphenyl ether PDA: p phenylenediamine DABA: 4, and 4'-diamino benzanilide: Pyromellitic acid 2 anhydride BPDA: 3, 4, 3', and 4'-biphenyl tetracarboxylic dianhydride BTDA: 3, 4, 3', and 4'-benzophenone tetracarboxylic dianhydride DSDA: 3, 3', 4, and 4'-diphenylsulfone tetracarboxylic dianhydride diamine DPE : [0050]
[Table 2]
Example of reference Acid 2 anhydride Diamine Mole ratio Viscosity Heat ray expansion coefficient (a) (b) (a) /(b) Pa-S x10-6/K B1 BPDA DPE DABA 20/80 20 18 B-2 BPDA DPE - 100/0 18 35B3 PMDA DPE PDA 50/50 15 20 B4 PMDA DPE PDA 70/30 24 24 B5 DSDA DPE PDA 90/10 20 39 B6 DSDA DPE- 100/0 16 50 [0051] On the belt made from stainless steel (width of face of 300mm) of the example 1 of an experiment - 10 (production of polyimide film of three-tiered structure) mirror-plane finishing, the polyamic acid film (about 25% - 35% of residual volatile matter contents) which serves as the 1st polyimide layer using the polyamic acid varnish shown in Table 3 or 4 was formed.
[0052] Next, about 25% - 35% of polyamic acid film residual volatile matter contents used as the 2nd polyimide layer was formed on this polyamic acid film, and the polyamic acid film (about 25% - 35% of residual volatile matter contents) used as the 3rd polyimide layer was formed further. The residual volatile matter content which sets three layers of polyamic acid films of the obtained three-tiered structure when it exfoliates from a belt was about 25% - about 35% (it is Table 3 and referring to Table 4 for details). Moreover, defects, such as foaming, were not observed, either.
[0053] The polyamic acid film of this three-tiered structure was heated all over the 170 to 350 degrees C continuous furnace of nitrogen-gas-atmosphere mind, it imide[ during 30 minutes ]-ized at 350 more degrees C, and the polyimide film of a three-tiered structure was obtained.
[0054] In addition, the polyimide film (Kapton 100H, Du Pont make) of a commercial monolayer was used as a polyimide film as an example 10 of an experiment.
[0055] To the front face of the polyimide film of the examples 1-10 of an experiment acquired example of experiment 11-20 (production of a flexible substrate), the plasma dry cleaning device (PX-1000, product made from March) was used, and surface treatment was performed by irradiating the argon plasma generated on the conditions of degree of vacuum 80mmTorr and RF output 120W. Subsequently, the DC magnetron sputtering method was applied to the processing front face, and the nickel/Cu alloy thin film of 150A thickness was formed in it from the nickel-Cu alloy (50% / 50%) target. Furthermore, Cu thin film with a thickness of about 1000A was made to form from Cu target. The same metal thin film as a polyimide film rear face was formed by the same technique if needed.
[0056] Next, thickness attachment of the Cu deposit with a thickness of 18 micrometers was carried out with electrolytic copper plating by having used the formed metal thin film as the electrode, and the conductor layer was formed. This obtained the one side or double-sided flexible substrate.
[0057] (Evaluation) About the polyimide film of the examples 1-10 of an experiment, it measured so that a "heat ray expansion coefficient" and "curl" might be explained below. Moreover, it measured so that the "bond strength" between a polyimide film and a conductor layer might be explained below about the flexible substrate of the examples 11-20 of an experiment in addition to a "heat ray expansion coefficient" and "curl." The obtained result is shown in Table 5 and 6.
[0058] It measured by the **** method (working loads 2.5g-5g) using the heat ray expansion coefficient measuring device (thermal mechanical analyzer (TMA/SCC150CU, product made from SII)) like the example A1 of measurement reference of a heat ray expansion coefficient.
[0059] The measurement polyimide film and flexible substrate of curl were cut down in the magnitude of 10cm around, and radius of curvature was computed from the average of the height of the four corners when carrying on a horizontal plate in the convex condition. Radius of curvature is wanted to be 200mm or more practical.
[0060] On the measurement conductor layer of bond strength, a liquefied resist (RX-20, TOKYO OHKA KOGYO CO., LTD. make) is applied, and negatives are dried, exposed / developed, and it etches in a ferric chloride water solution, a conductor pattern is created, and it is JIS. C6471 The bond strength when following and performing exfoliation 90 degrees was measured.

[0061]
[Table 3]
The example of an experiment 1 2 3 4 5 The 1st polyimide layer Polyamic acid varnish A1 A2 A3 A1 A3 Target thickness (micrometer) 2 2 2 2 2 Heat ray expansion coefficient (x10-6/K) 36 43 53 36 The 53 2nd polyimide layers Polyamic acid varnish B1 B1 B1 B3 B4 Target thickness (micrometer) 22 22 2222 25 Heat ray expansion coefficient (x10-6/K) 18 18 18 20 The 24 3rd polyimide layers Polyamic acid varnish A1 A2 A3 B-2 B6 Target thickness (micrometer) 22 22 2 Heat ray expansion coefficient (x10-6/K) 36 43 53 35 50 residual volatile matter content (%) 25.8 30.0 27.6 31.5 34.0 [0062]
[Table 4]
The example of an experiment 6 7 8 9 10 The 1st polyimide layer Polyamic acid varnish A1 A1 A1 B5 - Target thickness (micrometer) 2 2 2 2 - Heat ray expansion coefficient (x10-6/K) 36 36 36 36 - The 2nd polyimide layer Polyamic acid varnish B1 B1 B1 B1 - Target thickness (micrometer) 25 22 2222 - heat ray expansion coefficient (x10-6/K) 18 18 18 18 The - 3rd polyimide layer Polyamic acid varnish B4 B4 A3 B5 - target thickness (micrometer) 22 22 - Heat ray expansion coefficient (x10-6/K) 39 24 53 36-residual volatile matter content (%) 32.4 25.0 24.5 20.0 -[0063]
[Table 5]
Polyimide film Heat ray expansion coefficient Curl Example Noof observation thickness experiment. (x10-6/K) (radius of curvature mm) (micrometer) 1 19 Nothing (infinity) 26 2 22 Nothing (infinity) 25 3 24 Nothing (infinity) 26 4 23 Nothing (infinity) 26 5 29 it is (500 -- <) -- 27 Six 21 it is (500 -- <) -- 27 Seven 21 **** (<10) 26 8 20 **** (<10) 26 9 With no 21 (infinity) 26 10 22 **** (infinity) 26 [0064]
[Table 6]
Flexible substrate Polyimide film Conductor layer Curl example Noof bond strength experiment. Example Noof experiment. Forming face (radius of curvature mm) kgf/cm 11 1 Both sides Nothing (infinity) 1.85 12 2 Both sides Nothing (infinity) 2.00 13 3 Both sides Nothing (infinity) 1.70 14 4 One side Nothing (infinity) 1.80 15 5 Both sides Nothing (infinity) 1.65 16 6 One side Nothing (infinity) 1.90 17 7 (uniform conductor-layer formation is impossible because of curl size)
18 8 (Uniform Conductor-Layer Formation is Impossible because of Curl Size)
19 9 Both Sides Nothing (Infinity) 0.20 20 10 One Side **** (<200) 0.10 [0065] In the polyimide film which has the three-tiered structure of the 1st polyimide layer, the 2nd polyimide layer, and the 3rd polyimide layer from the above experimental result If the 1st polyimide layer arranged in the side which uses what has the heat ray expansion coefficient of a conductor layer and abbreviation identitas as the 2nd polyimide layer of those centers, and touches a conductor layer is constituted from sulfone radical content polyimide It can form controlling generating of curl for a metal thin film greatly with good bond strength according to a dry process on it.
[0066] Moreover, if the 3rd polyimide layer is also constituted from sulfone radical content polyimide, only on the 1st polyimide layer, also on the 3rd polyimide layer, it can form controlling generating of curl for a metal thin film greatly with good bond strength, and, therefore, the double-sided flexible substrate of a good property can be manufactured according to a dry process.
[0067] Moreover, the result of the examples 17 and 18 of an experiment shows becoming easy to carry out curl generating, when the difference of the heat ray expansion coefficient between the 1st polyimide layer and the 3rd polyimide layer becomes comparatively large.
[0068]
[Effect of the Invention] According to this invention, the adhesion between the polyimide film suitable for a flexible substrate and the metal thin film formed of a dry process on it can be raised, and it cannot be based on the contents of the heat history at coincidence, but generating of curl can be controlled.

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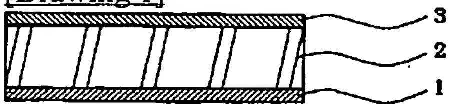
[Translation done.]

## DRAWINGS

[Drawing 1]




[Translation done.]